

THE LATERAL DISTRIBUTION OF POLYCYCLIC AROMATIC HYDROCARBONS IN ALLAN HILLS 84001 – IMPLICATIONS FOR THEIR ORIGIN. T. Stephan¹, D. Rost¹, C. H. Heiss¹, E. K. Jessberger¹, and A. Greshake², ¹Institut für Planetologie/ICEM*, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Str. 10, D-48149 Münster, Germany, stephan@uni-muenster.de, ²Museum für Naturkunde, Institut für Mineralogie, Humboldt-Universität zu Berlin, Invalidenstr. 43, D-10115 Berlin, Germany.

*Interdisciplinary Center for Electron Microscopy and Microanalysis

Introduction: Polycyclic aromatic hydrocarbons (PAHs) in ALH 84001 were considered as a major hint for relic biogenic activity on Mars [1]. Crucial for their proposed connection to early life forms is a suggested spatial association with carbonates that contain internal structures resembling terrestrial microfossils. Although each observation can be explained individually [2, 3] a lateral correlation would suggest a genetic link between PAHs and the microstructures.

A preliminary study of ALH 84001 by Thomas *et al.* revealed no clear correlation of PAHs and the so-called carbonate globules [4]. Three regions on a freshly fractured surface with a total size of $1 \times 0.5 \text{ mm}^2$ were found to be enriched in PAHs. Although a relationship seems to exist between the region with the highest PAH concentration and a carbonate spheroid, both other regions with enhanced concentrations of PAHs did not correlate with carbonates. On the other hand, not all carbonate globules in the analyzed sample contain PAH excesses nor even PAH concentrations above background.

Nevertheless, in a later work by the same authors, a spatial association of PAHs and carbonates was proposed and interpreted as a major clue to relic biogenic activity without presenting convincing new results [1]. Even in a recent paper, some of the authors still use the first study to claim that such a correlation exists [5].

Crucial for the investigation of spatial associations is the lateral resolution of the applied analytical methods. In the mentioned studies, microprobe two-step laser mass spectrometry ($\mu\text{L}^2\text{MS}$) was used for the analysis of PAHs. With this technique an unambiguous determination of a spatial association is limited by its lateral resolution, about $50 \text{ }\mu\text{m}$, a size that is comparable with the typical dimension of the carbonate globules.

Scanning transmission X-ray microscope (STXM) carbon mapping and X-ray absorption near-edge structure (XANES) spectroscopic measurements on carbonates from ALH 84001 indicated the presence of organic carbon (π -bonded carbon) within or associated with carbonate globules on the scale of $\sim 100 \text{ nm}$ [6]. A definite identification of the nature of this organic carbon, which seem to be locally present at percent levels, is not possible with these techniques. Only

a small fraction, less than 1 wt.-%, of the organic material in this meteorite may actually be represented by PAHs and there is isotopic evidence favoring a terrestrial origin for the majority of organic matter in ALH 84001 [7].

Analytical Technique: To investigate the actual distribution of PAHs in ALH 84001 on a sub-micrometer scale, we used time-of-flight secondary ion mass spectrometry (TOF-SIMS) with a lateral resolution of about $0.2 \text{ }\mu\text{m}$ to analyze areas on three different thin sections of ALH 84001 [8, 9]. This technique uses a time-of-flight mass spectrometer for the analysis of positive or negative secondary ions sputtered from the uppermost monolayers during primary ion bombardment. Besides atomic ions also large molecules survive the sputtering process, at least as characteristic fragments. Using a fine focused gallium liquid metal primary ion source, a simultaneous measurement of the lateral distribution for all secondary ion species with one polarity is possible. High mass resolution allows to separate atomic ions from hydrocarbons at same nominal masses.

Results: Our TOF-SIMS studies revealed PAHs on all three sections of ALH 84001, but in no case a correlation of PAHs with carbonates could be observed. In contrary, a general trend of a lower PAH concentration in carbonates compared to orthopyroxene or feldspathic glass seems to exist [8, 9].

Since the information depth in a typical measurement is of the order of a few atomic monolayers, surface contamination is a major concern in TOF-SIMS. The three investigated thin sections were prepared from three different pieces of ALH 84001 in two different laboratories minimizing the probability of a common contamination with external PAHs during sample preparation. A section of Chassigny [10] that was treated exactly like one of our ALH 84001 sections and measured directly before and after ALH 84001 contained no detectable PAHs. Therefore, contamination with PAHs not indigenous to the sample is unlikely.

On the other hand, redistribution of indigenous PAHs may occur during sample preparation, *e.g.*, polishing. This indeed was observed in one of our samples. For this section we observed first a rather uniform distribution of PAHs on the very surface. Af-

ter extensive sputtering with an argon ion beam that removed several atomic monolayers, the indigenous PAH distribution was revealed, showing the previously observed “anti-correlation” of PAHs and carbonates [9].

To understand the relative intensities of characteristic PAH mass peaks in the TOF-SIMS spectra [8], which vary significantly from those observed by $\mu\text{L}^2\text{MS}$ [1], we investigated with TOF-SIMS pure PAH substances, pentacene and coronene (Fig. 1), on silver substrates. Both substances showed fractionation during primary ion bombardment. Pentacene, being more susceptible to fractionation, revealed similar relative maxima, although in different proportions, in the mass spectrum as observed for ALH 84001. Differences from $\mu\text{L}^2\text{MS}$ spectra, especially the high abundance of low-mass PAHs observed by TOF-SIMS, can be explained by differences in ionization processes, e.g., stronger fractionation during ion bombardment. It is therefore plausible that spectra obtained by $\mu\text{L}^2\text{MS}$ and TOF-SIMS result from the same mixture of PAHs.

Discussion: A major question is still, where these PAHs, unambiguously present in ALH 84001, come from. Are they indigenous [1, 5] to this meteorite or were they acquired during residence in the Antarctic ice [3]? An important argument against their terrestrial origin is believed to be the reported decrease by a factor of 5–10 of the PAH signal towards the fusion crust of the meteorite [1, 5]. This decrease can at least in part be explained by different morphological properties of the fusion crust which has an inherently smaller surface area. If the PAHs observed in ALH 84001 result from terrestrial contamination and now reside along sub-micrometer sized fractions or grain boundaries, a correlation of PAH concentration

with internal surface area would be expected. From the TOF-SIMS measurements such a concentration along grain boundaries or sub-micrometer fractions can neither be confirmed nor ruled out.

Conclusions: Irrespective of their origin, a genetic link between PAHs and carbonate globules, the carrier of the so-called nanofossils, can be excluded from the lack of spatial association. Consequently these observations have to be taken individually and should not be considered collectively.

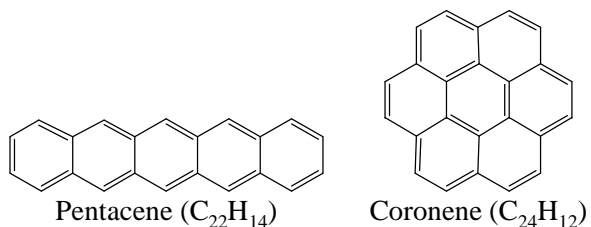


Figure 1: Pure pentacene and coronene samples were investigated on silver substrates using TOF-SIMS.

Acknowledgments: This work was supported by a special grant from the Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen.

References: [1] McKay D. S. et al. (1996) *Science*, 273, 491–504. [2] Bradley J. P. et al. (1997) *Science*, 390, 454. [3] Becker L. et al. (1997) *GCA*, 61, 475–481. [4] Thomas K. L. et al. (1995) *LPS XXVI*, 1409–1410. [5] Clemett S. J. et al. (1998) *Faraday Discussions (Royal Soc. Chem.)*, 109, 417–436. [6] Flynn. G. J. (1998) *Meteoritics & Planet. Sci.*, 33, A50–A51. [7] Jull. A. J. T. (1998) *Science*, 179, 366–369. [8] Stephan T. et al. (1998) *LPS XXIX*, #1263. [9] Stephan T. et al. (1998) *Meteoritics & Planet. Sci.*, 33, A149–A150. [10] Greshake A. et al. (1998) *LPS XXIX*, #1069.